Culture condition	Growth (μl pcv ml^{-1})	Chlorophyll content (μg ml^{-1})	Chlorophyll content (mg ml^{-1} pcv)	Ethane formation (nmol ml^{-1} pcv)	Proto-IX accumulation[a] (nmol ml^{-1} pcv)
At start	2.4	27.40	11.42	–	–
Control	3.6	33.3	8.98	nd[b]	2.45
Oxyfluorfen	3.4	5.30	1.56	13.38	106.43
(+) **1**	3.2	5.43	1.70	12.19	
(+) **2**	3.4	6.09	1.79	12.29	
(+) **3**	3.4	17.61	5.18	3.82	42.52
(+) **4**	3.6	12.18	3.38	11.00	
(+) **5**	3.2	8.30	2.59	10.83	
(+) **6**	3.2	16.18	5.06	10.00	
(+) **7**	3.4	6.22	1.83	11.47	
(+) **8**	3.2	26.85	7.46	n.d.	30.21
(+) Diuron	3.6	25.75	7.15	n.d.	32.44

[a] Proto-IX accumulation after a 2-h incubation.
[b] nd = not detected.

Table 3. Effect of 2-benzylamino-1,3,5-triazines (10^{-5} M) on the peroxidizing activity of oxyfluorfen in *Scenedesmus acutus* cells after 16 h incubation in the light

tory activity (pI_{50}) of compounds, as shown by the following equations:

$$\text{Ethane formation} = -3.834\ pI_{50}(\text{thylakoids}) + 29.366 \quad (\pm 1.902)$$

$[n = 7,\ r = 0.92,\ s = 2.03]$

$$\text{Chlorophyll content} = 1.742\ pI_{50}(\text{thylakoids}) - 5.587 \quad (\pm 0.789)$$

$[n = 7,\ r = 0.93,\ s = 0.84]$

REFERENCES

1 Kunert KJ and Böger P, *Weed Sci* **29**:169–173 (1981).
2 Böger P and Wakabayashi K, *Z Naturforsch* **50c**:159–166 (1995).
3 Ohki A, Ohki S, Koizumi K, Sato Y, Kohno H, Böger P and Wakabayashi K, *Nihon Noyaku Gakkaishi (J Pestic Sci)* **22**:309–313 (1997).
4 Koizumi K, Kuboyama N, Tomono K, Tanaka A, Ohki A, Kohno H, Böger P and Wakabayashi K, *Pestic Sci* **55**:645–646 (1999).

Steric structure–activity relationships of the rice blasticide, S-2900 (diclocymet)

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Abstract: The four diastereomers of 2-cyano-*N*-[1-(2,4-dichlorophenyl)ethyl]-3,3-dimethyl-butyramide were prepared by a direct HPLC separation with chiral columns. The [*(S)*acid, *(R)*amine]-isomer (was the most antifungal among the diastereomers tested. Because of the lability of the clinical group in the acid moiety, the (*RS)*-(*R*)-isomer is being developed as a rice blasticide. (S-2900, proposed common name diclocymet).

Keywords: S-2900; rice blasticide; optically active diastereomer

During the course of a study on modifications to the structure of the herbicide bromobutide (Fig 1; **1**),[1] we found that its cyanobutyramide derivatives are effective in controlling rice blast disease caused by *Pyricularia oryzae* Bri & Cavara. Of these, 2-cyano-*N*-[1-(2,4-dichlorophenyl)ethyl]-3,3-dimethylbutyramide (**2**) was selected as a potential new rice blasticide. The molecule has two stereogenic centres, one in the acid and one in the amine moiety. To examine the steric structure/biological activity relationships of the molecule, the four possible stereoisomers were prepared by optical resolution of 1-(2,4-dichlorophenyl)ethylamine followed by column chromatographic separation or by recrystallization of the optically active diastereomeric mixture of the cyanobutyramide. In particular, the racemic diastereomers could be separated cleanly using HPLC with chiral columns such as Sumipax YMC-Gel and Sumichiral OA-4700. The absolute configuration of one of the diastereomers, mp: 180–186 °C, $[\alpha]_D = +45.9°$, was determined to be the *(R,R)*-configuration by X-ray single crystal analysis.

As shown in Table 1, the diastereomers with an *(R)*-configuration at the amine moiety exhibited considerable antifungal activity, while those with an *(S)*-

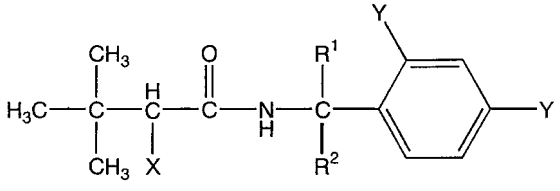

Figure 1. Structures of compounds discussed. Bromobutide **1**: X = Br, Y = H, $R^1 = R^2 = CH_3$; **2**: X = CN, Y = Cl, $R^1 = CH_3$, $R^2 = H$.

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Table 1. Preventive activity of the stereoisomers of 2-cyano-*N*-[1-(2,4-dichlorophenyl)ethyl]-3,3-dimethylbutyramide.[a]

	Activity[b] at concentration (mg litre^{-1})					
Isomer	6.3	3.1	1.6	0.8	0.4	0.2
(R, R)	3	2	2	1	0	
(S, S)	0					
(R, S)	0					
(S, R)	4	4	4	3	3	1
(RS, R)	4	4	3	3	2	0
(RS, RS)	4	3	3	2	1	0

[a] Pot test with rice blast disease.
[b] 4; >90, 3; 70–89, 2; 50–69, 1; 30–49, 0; <29% control.

configuration at the amine moiety were inactive. The [*(S)*acid, *(R)*amine]-isomer was the most active, both in inhibiting fungal melanin biosynthesis *in vitro* and in pot tests on rice blast disease.

Racemization at the C-2 position of the acid moiety bearing the cyano group proceeds easily under basic conditions. Thus, the compound having the *(RS)*-configuration at the acid and the *(R)*-configuration at the amine moiety and containing enolizable hydrogen at the C-2 position of the acid is being developed as a new rice blasticide (S-2900, proposed common name diclocymet). It should be added that some related amides with an *(S)*-configuration at the amine moiety have been reported to be more herbicidal than bromobutide.[2]

REFERENCES

1 Kirino O, *Nihon Noyaku Gakkaishi (J Pestic Sci)* **9**:571–579 (1984).
2 Kirino O, Takayama C and Inoue S, *Nihon Noyaku Gakkaishi (J Pestic Sci)* **12**:79–84 (1987).

Synthesis and juvenile hormone activity of benzimidazolylterpenes possessing a 2,7-dimethyloctane skeleton

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Abstract: Benzimidazolylterpenes, possessing a 2,7-dimethyloctane skeleton showed IGR-activity on pupae of *Tenebrio molitor* L in laboratory tests: *N*-(7-methoxy-2,7-dimethyl-2-octenyl)benzimidazole showed the greatest activity.

Keywords: benzimidazolylterpenes; juvenile hormone activity

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1 INTRODUCTION

Most of the insect growth regulators (IGRs) with juvenile hormone (JH) activity known to date are derived from monoterpenes and sesquiterpenes. Several imidazolyl- and benzimidazolyl monoterpene derivatives have shown anti-juvenile hormone activity in larvae of the silk worm, *Bombix mori* L.[1,2] Industrial production of terpene and sesquiterpene derivatives is a very expensive process and this limits the use of IGRs in agricultural practice. We have prepared *N*-monoterpenyl benzimidazoles, having the terpenyl moiety differing from that in natural terpenes in the position of methyl substituents and in the position of the double bond of main chain, i.e with a 2,7-dimethyloctane skeleton (eg **1** Fig 1). Such terpene derivatives can be synthesized by one-pot synthesis from isoprene. We prepared *N*-(2,7-dimethylocta-2,7-dien-1-yl)-benzimidazole (**2**), *N*-(2,7-dimethylocta-1,7-dien-3-yl)benzimidazole (**3**) and *N*-(7-methoxy-2,7-dimethyl-2-octen-1-yl)benzimidazole, (**1**) and tested them for IGR activity.

2 EXPERIMENTAL

2.1 Synthesis

The general procedure was palladium-catalysed allylic alkylation of benzimidazole with a tetra-alkyl ammonium salt (Fig 1; Scheme 1). The chosen salts were *N*-alkyl-*N*-methylpiperidinium iodides. The details of the syntheses of **2** and **3** have been published.[3] Compound **5**, the intermediate for **1**, was prepared as shown in Fig 1, Scheme 2. The alkyl piperidine (**6**) was prepared from isoprene and piperidine by a previously described method[4] and allowed to react with methanol in the presence of acid. The resulting amine (**7**) was converted into the *N*-alkyl-*N*-methylpiperidinium salt (**5**) by reaction with methyl iodide. Allylic alkylation of benzimidazole by **5** was achieved by catalysis with $Pd(dba)_2$. Compound **1** was produced in admixture with 5% of the product of allylic rearrangement.

2.1.1 N-(7-Methoxy-2,7-dimethyl-2-octen-1-yl)piperidine (7)

Perchloric acid (570 g litre^{-1}; 21.6 ml) was added dropwise to solution of amine **6** (7.2 g; 32.5 mmol) in methanol (22 ml) and the mixture was heated under reflux for 14 h. Sodium hydroxide in methanol (150 g litre^{-1}; 50 ml) was then added and the methanol removed under vacuum. The residue was diluted with water, extracted with benzene and the organic phase was dried (sodium sulfate). Removal of the benzene and fractional distillation of the residue gave amine **7** as a colourless oil; yield: 5 g (61%); bp 107–109 °C/